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Phase contrast studies at extremely small refractive differences in liquids

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With 2 figures in the text

General remarks

As far as is known (1), no one has hitherto tried to use phase contrast methods for an extensive study of refractive index differences in fluids, as for example the comparison of solutions of different concentrations, except when using phase-contrast microscopes for detailed work. This lack of progress is due partly to the novelty of the whole field, and partly to the many experimental difficulties connected with such studies. Estimating 50 A as a provisional sensitivity limit in this application, which no doubt can be decreased since it is due to technical and not to fundamental reasons, freedom from internal strias and exactness in the shape and microstructure are demanded in the optical parts near the fluid to such an extent that the sum of all errors is below that amount, and for the aberrations and zonal errors, an amount of not much greater value. Moreover, accidental irregularities in the fluids themselves, as can arise from random temperature fluctuations, may very easily mask the wanted effects. As will be shown in this short report, such applications are, however, possible, and are useful for a series of physical and chemical investigations.

Constructional details

A slit system, not a point or ring system, is preferable on account of the types of application for which the apparatus is intended, and it also facilitates the construction of a well-defined phase-shifting device. Further, monochromatic light is necessary: we have used Hg 5461 A. The liquid to be examined should be kept in a cell of very uniform thickness and with a rather large aperture. As this cell must be closely connected to the optical system imaging the entrance slit onto the phase plate, it is best constructed from two planoconvex lenses, in order to reduce the number of optical elements, especially optical surfaces. As shown in Fig. 1, the two lenses form a cell for the fluid, the details of which can be varied in many ways. The lenses have a square outline, 80 × 80 mm, and the focal distance of the compound system is about 850 mm. The lenses were manufactured by the Svenska Aktiebolaget Gasaccumulator. They are free from striae above a few tens of A, and their polish shows a profile depth according

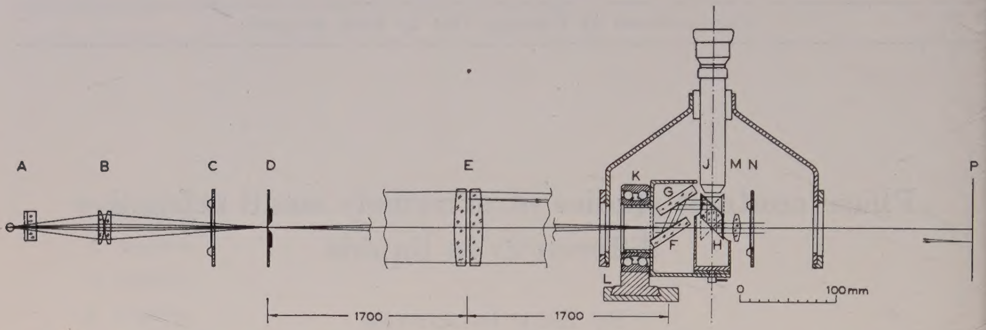

Fig. 1. Optical arrangements. *A* mercury lamp with filter, *B* condenser, *C* first polaroid, *D* entrance slit, *E* lens system, also cell for the liquid, *F* phase mirror, *G* additional aluminized mirror, *H* rhombic prism, *J* microscope focussed on *F*, *K* ball bearing, *L* slide, *M* objective, *N* second polaroid, *P* image plane.

to a multiple-interference test (2) not exceeding 10 A. Although their spherical aberration for this geometry causes a small variation of illumination within the field, for the most sensitive adjustments (it was not practical to increase the focal length further), they are very suitable to the present work.

The phase-contrast device is the FRANÇON-NOMARSKI mirror (3), constructed in the manner previously described (4), or the inverted type of mirror introduced by the author (4). An effort has been made to include in the phase mirror device such optical and mechanical details as are necessary to make rapid adjustment possible without loss of stability. The construction is such that the whole device can be rotated round the incident central ray, which coincides with the exit ray. Thus, the phase plate *F* is followed by a parallel aluminized mirror *G*, which throws the light onto a rhombic prism *H*, so that the light is restored to its original direction. The parts *F*–*H* are contained in a rigid unit, which may be rotated in a double-row and angular-contact ball bearing, the whole being mounted on a slide which is movable in a direction perpendicular to the optic axis. The micrometer drive adjusting the turning, and the micrometer for the displacement of the mirror *F* perpendicular to the rays, are not shown in the figure. For the rapid and frequent adjustment of the device with respect to the image of the slit *D*, the prism *H* is rotatable through 180° around its vertical axis. Its upper, aluminized surface is then in the position indicated by the dotted lines, and the centre of the mirror *F*, with the slit, is viewed by the long-distance working microscope *J* (NIFE type BrT 20-S).

The possibility of rotating the phase-contrast device is important, not so much in these applications on liquids, but when it is being used for schlieren photographs of wind tunnel fields, where it can be adjusted parallel to a wave front from a supersonic flow.

Preliminary studies of refractive differences

Assume that the adjacent surfaces of the lenses *E*, set parallel, form the borders of a fluid with the refractive index n_1. In one relatively narrow horizontal strip another fluid, possessing the refractive index n_2, is inserted. The thickness of this strip in the direction of the optic axis is called t, which is mostly the entire distance between the surfaces, but may be less. The difference in optical path Δ between rays traversing the two fluids is

$$\Delta = (n_2 - n_1) \cdot t \tag{A}$$

This corresponds to an angular phase difference in the exit wave front, equal to Δ divided by the air wavelength and multiplied by 2π.

For applications on diluted water solutions, the excess of refraction, $n_2 - n_1$, of the solution over the solvent, for many fluids follows the proportionality law

$$n_2 - n_1 = r \cdot z, \tag{B}$$

where z is the relative concentration with respect to a standard concentration c_0, say 1 per cent, and r is a constant, the specific refractive index for the solution in question.

For the experiments hitherto performed, the author has used inorganic salts, such as chlorides, and also glycine (amino-acetic acid), which is known to follow the proportionality law (5) and has the advantage of a relatively large diffusion constant. As c_0 we adopt the 1 per cent solution, or, more precisely, 1 gram of substance in 100 cm^3 of solution. The value of r, found by calculation using the extensive interference data given in (5), is $r = 2.44 \cdot 10^{-3}$. According to (A) and (B), a sensitivity of 50 A corresponds, for a cell with $t = 10$ mm, to a refractive index of $0.5 \cdot 10^{-6}$ and a z of $2 \cdot 10^{-4}$, i.e. 0.0002 per cent.

Influence of temperature. When measuring such small quantities, one must take into consideration all kinds of disturbances, especially those connected with temperature. Fortunately, the temperature coefficient of refractive index of water has the low value of $dn/dt = -9 \cdot 10^{-5}$. In order to correspond to the limit of detectable refractive indices, the uniformity of temperature within the same area of the optical field should be within 0.006 degrees. There is no need, however, for random striae in the liquid to fulfil this condition, as they are never sufficiently extended to fill the whole thickness t, being generally about a tenth of it. A constancy of a few hundredths of a degree is sufficient. This should be considered when constructing the cells. On account of the large heat capacity of the lenses used here, the temperature is uniform to the extent that random striae are too small to be detectable in the phase contrast field. Thus, it has not been necessary up to now to include a special thermostat.

Temperature fluctuations on account of intentional mechanical movements, as is described below, or of dilution heat at the borders between solution and solvent, can be shown to be of negligible influence.

Technique of forming defined liquid fields. Every insertion into the image field of walls, or similar boundaries, complicates the method, since they interfere with the phase-difference interference and make the evaluation more difficult. In work done up to now, consequently, the practice has been to present the liquid n_2 in the image area in other ways than enclosing it in a separate cell. The liquid n_1 was distilled water, and solution n_2 was made up with water from the same store. The cell was constructed as shown in Fig. 2 a, the borders being rubber tubes pressed together. From the left the tube of an injection

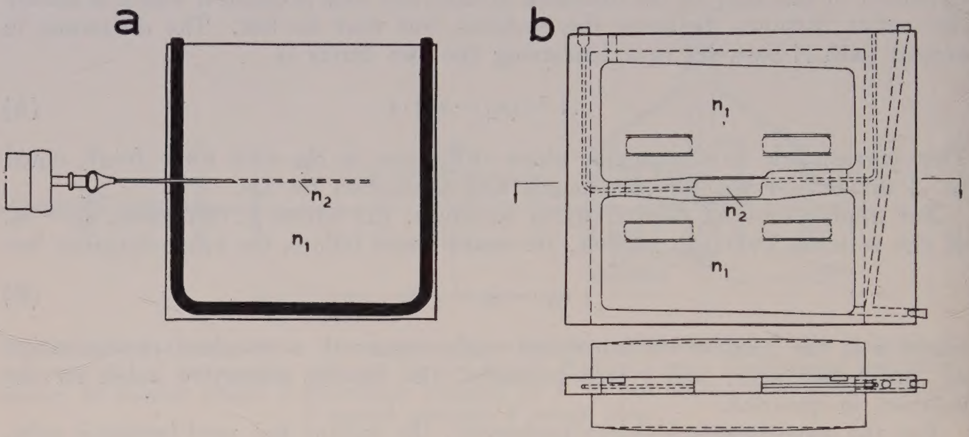

Fig. 2. Construction of the cell: *a* arrangement for preliminary studies, with injected liquid *b* compound cell for stationary liquid, the four spots around the central cell acting as phase difference references. *Note added in proof:* In the meantime, the *b*-construction has been changed; reference spots are now placed in the central vertical field above and below n_2. See (9).

syringe as used in medicine is inserted. The thickness of the cell was 2.8 mm, and the tube diameter, which corresponds to the value t when the liquid n_2 is forced through it, 0.44 mm. Sometimes, drops from the liquid n_2 were allowed to fall into the liquid, their diameters being measured within 0.1 mm.

Before a ray of the liquid n_2 is forced into the n_1 liquid, it must remain long enough in the syringe tube to equalize temperature to within some hundredths of degrees. The ray then enters the cell, and its image in phase contrast near the mouth of the tube is studied. When injected with proper speed, the ray will be straight and uniform in its first part, and then bend off in a clearly visible manner. In order to check the method, glycine solutions of $z = 0.010$ and 0.002 (per cent) were injected. The former was well visible and, as described below, its light contrast could be quantitatively estimated. Also the ray from the more dilute solution was visible but not measurable visually, the path difference being about 25 A; drops with larger equivalent t from this solution were well visible, standing out strongly from the background.

This result is in agreement with that calculated for the phase-contrast device under the conditions of polarization used. A more direct and safer method is, however, to introduce standard phase-contrast striae into the image field in order to measure relatively to them.

Standard striae as references for optical paths. Close to the cell system E is placed a plane-parallel glass provided with a parallel set of standard striae, the glass being placed so that these striae are parallel to the slit and to the liquid ray, i.e. horizontally. The striae consist of magnesium fluoride, evaporated in vacuo to controlled thickness, which are measured with the method of multiple beam interferences (4). From the thickness, the optical path differences introduced by them were calculated, as $(n - 1)$ times the thicknesses, since n is known to be well reproducible ($n = 1.38$) for magnesium fluoride. The striae, equivalent to path differences of 45, 55, 70, 80, 100, 115, 420, and 600 A, were all visible, although the image was slightly disturbed by random striae in the the glass. The injected ray from the n_2 solution, $z = 0.01$, was estimated to be most closely equivalent to the standard stria of 115 A. The Δ calculated from (A) and (B) for the centre of the ray is 107 A; a closer agreement is not to be expected, since these are only visual estimations, and the geometry of the two striae differ.

Difference refractometers with a sensitivity of 10^{-6} in refractive index

It is obviously possible to arrange refractometers with sensitivities better than those obtainable with ordinary interference methods. Fig. 2 b shows a model now under construction for stationary fluids. The liquid n_2 is enclosed in the central cell, the reference liquid n_1 being contained in the rest of the cell. The central cell must be dimensioned so as to correspond to the requirements of the phase-contrast method. Firstly, the height of the cell must be small with respect to that of the whole image, so as to correspond to a diffraction pattern sufficiently large in respect to it, and further, the interferences from the walls must not severely influence the intensity of the phase-contrast image of the central cell in its central part where it should be measured. The whole problem has not been theoretically treated, but preliminary experiments indicate that the dimensions chosen give a satisfactory result. The central cell contains about 1 cm^3 of fluid. It is surrounded by a series of standard patterns of the same geometry, consisting of magnesium fluoride evaporated onto the outer surface of one of the lenses to controlled, different thicknesses. The image field is measured photoelectrically, or photographed, the value of $n_2 - n_1$ being obtained by interpolation of light intensities.

Another device, now under construction, is more sensitive and can work with less material, but has the disadvantage that the liquid is lost. An arrangement, in its principle ressembling that of Fig. 2 a, consists of a slit of a few tenths of 1 mm in height, but extended over the whole thickness t of the cell (about 10 mm). The liquid n_2 is injected, and its image is photographed with a synchronized camera at a suitable time after the injection of the ray. Standard striae of the same height as that of the slit are mounted in the field near and parallel to the ray. With this method, the necessary amount of liquid n_2 can be limited to 0.1 cm^3, and the accuracy of the determination is estimated to be below 10^{-6}.

Application to the system $D_2O - H_2O$

As the difference of refractive index of D_2O and H_2O is, (6), for z being the mole fraction of the compound, $r = 4.73 \cdot 10^{-3}$, we can calculate that the limit given above for the accuracy of the method corresponds to an analysis of a composition of this compound to about 10^{-4}, i.e. 0.01 mole fraction per cent. When larger amounts than some tenths of 1 cm^3 are available, this accuracy ought to be still more improved.

Applications to boundaries

It ought to be kept in mind that this method is not restricted to the minor phase differences of hundredths or less of wavelengths that have been treated here. Especially with attenuation of the diffracted light (4), it can also be used with advantage over many wavelengths, and thus the sensitivity can be regulated according to circumstances. Therefore, it can in many applications replace interference methods, which are more complicated technically, and can extend them to greater sensitivity in the sub-wavelength region. The author has studied, for example, the diffusion boundary between a 1 per cent water solution of glycine and pure water. The fringes are contrasty, positions and intensity variations corresponding to the Gaussian curve. This method is most suitable for the study of boundaries under certain conditions to be discussed in a later paper, and may be used to complement methods using various interferometers (5, 7, 8) in the study of boundary effects, such as diffusion and electrophoresis, especially when only small amounts of substance or dilute solutions are available.

Work is in progress on the methods described here.

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